Vapour deposition of poly(alkyl-2-cyanoacrylate) resist coatings: a new electron-beam/deep-ultra-violet photoresist technology

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Alkyl-2-cyanoacrylate (CA) polymers are of interest as microlithographic photoresists for the production of submicrometre semiconductor devices owing to their high sensitivity to electron beams and X-rays. Solutions of the polymers tend to be unstable, however, which has limited their use in this area. Furthermore, the polymer films spun from solution have not shown any improvements in dry etch resistance over poly(methyl methacrylate), the standard resist used for electron-beam/X-ray work. Recently we have found that if the CA resist film is grown by a new vapour-deposition polymerization technique, directly onto the semiconductor substrate, then films with excellent dry etch resistance and high sensitivity can be produced. The method avoids the use of solutions, allows thick films to be deposited for ion implant masking and exhibits excellent uniform step or conformal coverage for non-planar technologies.

(**Keywords:** poly(alkyl-2-cyanoacrylate); vapour deposition; photoresist; electron beam irradiation)

INTRODUCTION

Polymers derived from alkyl-2-cyanoacrylate monomers have been used for about 30 years as structural adhesives capable of bonding a wide variety of substrates, including metals, plastics, rubbers, glass and wood[1]. They are also used as tissue adhesives in certain surgical operations where sutures are not desirable or possible. More recently they have attracted attention as polymeric binding agents in controlled drug delivery systems[2]. The commercially important cyanoacrylate monomers are unsubstituted C_1-C_4 alkyl esters (e.g. methyl, ethyl, allyl, etc.). The materials polymerize extremely rapidly at room temperature, initiated by bases including covalent compounds such as amines and phosphines[3]. Weakly basic materials such as polar solvents, halide ions and even trace amounts of water have also been reported to be catalysts for polymerization[4,5]. Under ambient conditions the polymerization proceeds by a 'living'-type anionic or zwitterionic mechanism unaffected by conventional terminators of anionic polymerization, such as water or oxygen[6]. The unique reactivity of cyanoacrylate monomers has been attributed to resonance stabilization of the propagating anion by the electronegative nitrile (–CN) and ester (–COOR)

groups[1]. As adhesive compositions, they harden in typically a few seconds when placed between two adherends, giving structural joints with ultimate shear strengths in the range 1–25 MPa (ref. 1). The polymers are relatively unstable towards a variety of chemicals, including alkaline solutions and certain solvents such as acetonitrile and dimethylformamide (DMF)[6,7]. Thermal stability is also relatively low with quantitative conversion to monomer occurring at temperatures in excess of about $120°C$[8]. While these features have limited the use of cyanoacrylate polymers to relatively benign environments, they can be considered beneficial in areas where the polymer performs only a temporary function, for example, photoresists.

Several reports on the use of solutions of poly(alkyl-2-cyanoacrylates) as microlithographic resists have appeared[9-12] and, while this work has shown that the polymers offer benefits in terms of sensitivity and contrast, they have not been employed in the fabrication of electronic devices. This is due mainly to storage instability of the polymer solutions in common solvents[7,13] and general difficulties related to the processing of the resist solutions. Recently, however, we have developed a new method for the deposition of cyanoacrylate polymer resist layers directly from monomer vapour, which avoids the problems associated with spun-on films from polymer solutions[14]. In addition to obtaining the expected benefits in sensitivity and

contrast, the vapour-deposited films have improved plasma etch resistance over equivalent poly(alkyl-2-cyanoacrylates) spun from solution.

## EXPERIMENTAL

Monomer synthesis

Alkyl-2-cyanoacrylate monomers were prepared by the base-catalysed condensation of the corresponding alkyl cyanoacetate with formaldehyde followed by de-polymerization at high temperature according to standard procedures[15] and used for vapour deposition after a single distillation.

Polymer synthesis

The polymers were prepared by the zwitterionic polymerization of monomer with triphenylphosphine as initiator in acetone and precipitated with acidified methanol[16]. Resist solutions were prepared by dissolving polymer (10%) in freshly distilled and dried CH_3NO_2. The polymer solutions were filtered through a 0.5 μm Teflon filter.

Vapour deposition

A vapour-deposition chamber was constructed as shown in *Figure 1*. A shallow bath of cyanoacrylate monomer was heated in a small chamber into which a silicon wafer was introduced on a sliding holder with the polished side facing the monomer pool. The surface of the wafer was preactivated by spinning a solution of 10% N,N,N',N'-tetramethylethylenediamine (TMED) in hexamethyldisilazine (HMDS) onto the surface (50 s at 4000 rpm). (Alternatively the surface may be activated by exposure to TMED vapour or by dipping the wafer into the amine solution.)
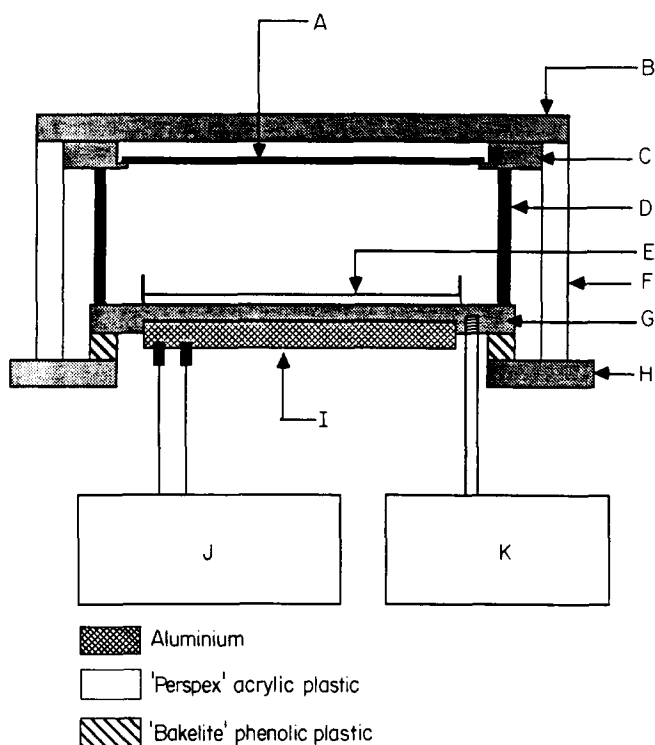
Figure 1 Schematic cross section of vapour-deposition chamber: A, 3 inch silicon wafer; B, lid; C, sliding substrate holder; D, cylindrical plastic flow guide; E, monomer pool; F, Perspex sides; G, hot plate; H, base; I, heater; J, variable transformer, 0–200 V; K, digital temperature display

Resist evaluation

Film thickness was determined using a Nanospec measurement system. Electron-beam (E-beam) lithography was carried out using a Jeol 35CF scanning electron microscope which had previously been adapted to permit lithographic evaluation. An 0.1 μm beam diameter was used to write the pattern in a vector-scan mode. Plasma etching tests were performed in a planar plasma etching system operating with a 12:5:4 mixture of $Ar:CHF_3:CF_4$ at a pressure of 8 Torr and a power density of 200 mW cm^{-2}.

Molecular-weight measurements

Estimations of number- and weight-average molecular weights and molecular-weight distributions were determined by gel permeation chromatography, using a Waters 501 model high-pressure liquid chromatograph equipped with a differential refractometer detector. Tetrahydrofuran was used as eluent for poly(n-butyl-2-cyanoacrylate) and acetone for poly(ethyl-2-cyanoacrylate) with a flow rate of 1 cm^3 min^{-1}. A Waters 'Ultrastyragel' mixed-bed column with a linear performance over the range 2000–4000000 molecular weight was employed. The molecular-weight calibration curve was obtained using standard poly(methyl methacrylates) from Polymer Laboratories Ltd.

RESULTS AND DISCUSSION

The vapour process

The vapour-deposition process is shown schematically in *Figure 2*. Inactive semiconductor substrates were activated to initiate cyanoacrylate polymerization by spinning a solution of amine onto the surface. The residual amine was completely removed in a N_2 stream to restore the mirror finish of the polished surface. It was not possible to detect a measurable film thickness after activation, which indicates that 'film' thickness is less than 10 nm (limit of Nanospec). It is probable that activation results in a surface modification rather than film deposition since the amines employed are quite volatile at room temperature. Alternatively, activation can be achieved by exposing the surface to amine vapour in a closed container or by dipping the wafer in a basic solution. The process appears to be general for amines and in addition to TMED and HMDS both N,N-dimethyl-p-toluidine and 3-aminopropyltriethoxysilane have been successfully employed.

Following activation the wafers were exposed to cyanoacrylate monomer vapour in the vapour chamber described above. A polymer film immediately forms and grows uniformly and at constant rate depending on the monomer temperature and exposure time (deposition time) to the vapour. *Figure 3* shows the effect of increasing temperature on the film thickness for 60 s exposure to monomer vapour. The thickness varies linearly with temperature over the range 40–70°C. This suggests that the monomer flux incident on the substrate depends on the monomer saturation vapour pressure within the chamber rather than on the evaporation rate of the monomer. Above 80°C the deposition was unpredictable and gave uneven films due to liquid condensation. For a fixed monomer temperature the deposited film thickness varies linearly with time (*Figure 4*). Relatively thick layers of resist may be grown during a single deposition (up to
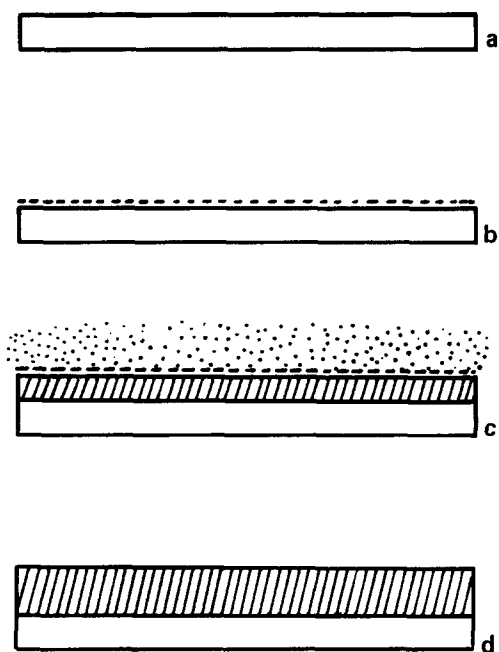
Figure 2 Schematic representation of vapour coating process: (a) clean unactivated substrate; (b) activated substrate; (c) growing polymer film with active front in contact with monomer vapour; (d) fully grown resist layer
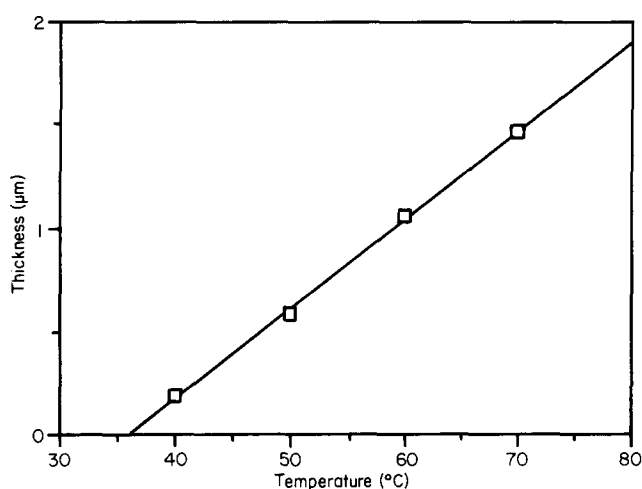

Figure 3 Film thickness as a function of monomer temperature for 60 s exposure to monomer vapour
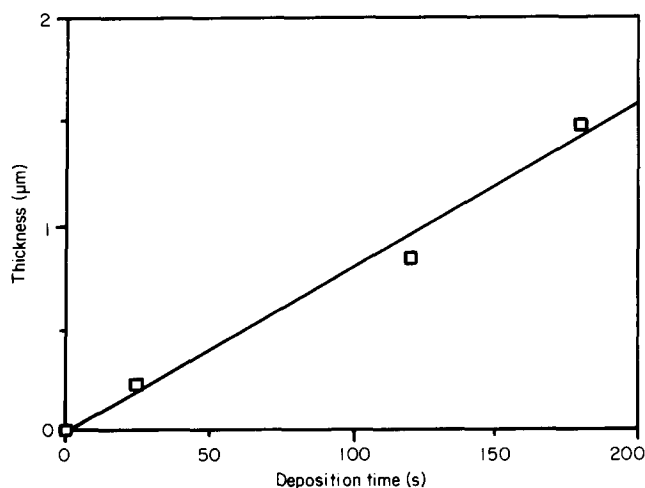
Figure 4 Film thickness as a function of deposition time (i.e. exposure time of substrate to monomer vapour) at a monomer temperature of 50°C

7 μm), which makes the process particularly attractive for masking in ion implantation or ion beam milling operations.

The formation of thick films suggests that the active polymerization initiation sites are transposed from the substrate surface to the growing polymer front (*Figure 2c*). This interpretation is consistent with the living zwitterionic polymerization mechanism proposed by Pepper[17] and is confirmed by the observation that the deposited polymer remains active for a reasonable period of time following deposition. Activation renders the surface sufficiently basic to initiate polymerization. The exact nature of the initiator groups (or sites) is in most cases still unclear, but may result from an adsorbed monolayer of amine (or ammonia in the case of HMDS) at adsorption sites on the surface. In the case of amines containing hydrolysable silanes, the basic initiator groups can be expected to form covalent bonds with free hydroxyl groups of the silicon oxide outer layer[18] (*Figure 5*). Alternatively, activation may result in the formation of various surface silicate anions by a 'neutralization' reaction with the basic activator. Anions of certain weak acids are already known to be initiators of cyanoacrylate polymerization[4]. Whichever process occurs, basic groups associated with or bound to the surface would then be expected to initiate polymerization by the already proposed zwitterionic mechanism[17]. The growth of the polymer at the surface occurs at a solid/vapour interface without liquid condensation occurring. Chain termination probably involves proton transfer from water with
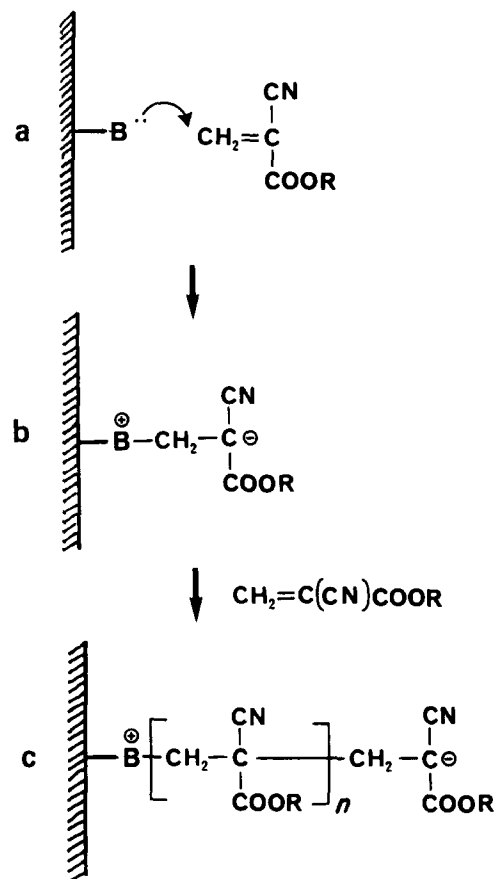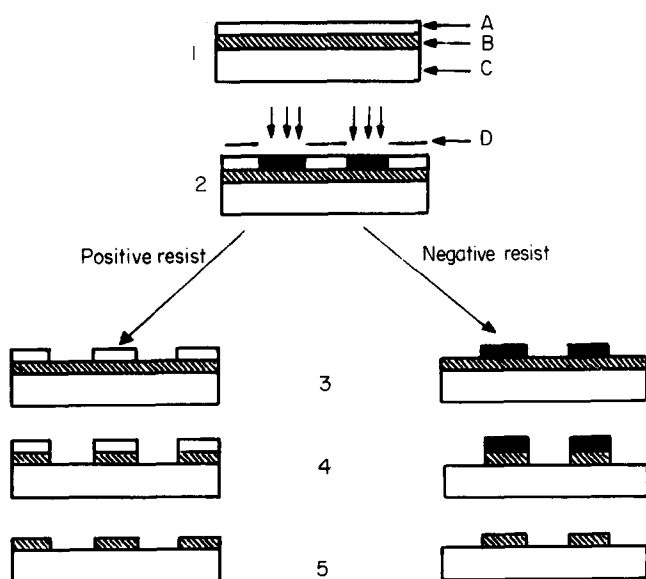

Figure 5 Proposed mechanism of cyanoacrylate polymerization on activated surface. Initiator site or group located on substrate surface adds to monomer at solid/vapour interface (a) to form initiating zwitterion (b) which adds subsequent monomer units via macrozwitterionic propagating species (c)

the generation of hydroxyl anion[4], which re-initiates by an anionic mechanism ensuring little or no disruption to the kinetic sequence. This results in the formation of a densely packed, thick polymer film.

A preliminary molecular-weight analysis of vapour-deposited poly(ethyl cyanoacrylate) and poly(n-butyl cyanoacrylate) polymers was carried out by g.p.c. The polymers were prepared by deposition onto a 3 inch silicon wafer followed by removal of the film in a suitable solvent. The process was repeated until sufficient polymer was collected. The combined solutions were concentrated to ensure adequate detection (r.i.). In all cases the chromatograms showed a high-molecular-weight component with $\bar{M}_n$ between 1×10^6 and 2×10^6 and one or more lower-molecular-weight components with $\bar{M}_n$ of 5000 or less. The high-molecular-weight fraction was found in the cases examined to have a MWD $(\bar{M}_w/\bar{M}_n)$ in the region 1.1 to 1.5. These values would suggest that vapour deposition provides polymers with significantly narrower distributions than have been obtained for solution-polymerized material of comparable molecular weight[9,19]. The low-molecular-weight components are thought to be due to polymer degradation which occurs in solution[13] and may not be present in the solvent-free vapour-deposited film. The lithographic sensitivity and contrast of a polymeric resist film are expected to improve with increasing molecular weight and decreasing distribution[20] and our results in this area (detailed in the following section) would support a polymer with comparatively high molecular weight and narrow MWD.

Lithographic properties of vapour-deposited cyanoacrylate polymers

In the fabrication of microelectronic devices, lithography is used to form patterns in a layer of resist. The lithographic process is illustrated in *Figure 6*. A thin uniform layer of polymer is applied to the substrate, usually by spinning from solution. The resist is then selectively exposed to u.v. or X-ray radiation through a mask or by steering a tightly focused beam of electrons or ions to generate the required pattern. After exposure, an image is developed in the resist using a developer solution which removes exposed polymer in the case of a positive resist and unexposed polymer in the case of a negative resist. The patterned substrate is then processed (etched, metal-coated, doped, etc.) to alter selectively the electrical properties in the exposed areas. During this process the patterned polymer functions to 'resist' the action of the process step.

For a polymeric film to function as a viable resist, it should exhibit good sensitivity to the exposing radiation, so that adequate throughput can be achieved. It should also be capable of generating highly resolved feature sizes with sharp profiles and be resistant to a range of chemical and plasma etchants. The vapour-deposited poly(cyanoacrylate) resist has been evaluated in terms of these parameters, using E-beam radiation and compared with both poly(cyanoacrylate) and poly(methyl methacrylate) (PMMA) resists, which were prepared in the conventional manner by spinning a solution of the polymer onto the semiconductor surface. Sensitivity and contrast were determined by exposing a pattern of four squares $(40 \times 40 \, \mu m)$ to varying electron doses and developing the image. The thickness of the resist remaining in the exposed area was measured in all cases and the average value taken. The normalized thickness (NT) was calculated from the ratio of resist thickness after development to original thickness, and plotted against electron dose. The cyanoacrylate resists were found to have curves characteristic of other positive resists where NT remains constant up to a certain dose and then begins to decrease with increasing dose, finally falling to zero (i.e. complete removal of the resist). The transition region of the curve has a linear section which, when extrapolated to intercept the X-axis, defines the resist sensitivity for the particular processing conditions.

The sensitivity curves for vapour-deposited poly(ethyl cyanoacrylate) at 0.5 and 1.0 μm film thickness are illustrated in *Figures 7* and *8*. The sensitivity values determined from these data were 19 and 15 $\mu C \, cm^{-2}$, respectively. *Figure 9* shows the curve for a 0.6 μm thick film of the same polymer applied from solution. The sensitivity in this case was found to be 21 $\mu C \, cm^{-2}$. These results suggest that the mode of deposition (vapour or solution spinning) has little or no influence on sensitivity. By comparison, the sensitivity measured for spun PMMA was found to be 54 $\mu C \, cm^{-2}$. The cyanoacrylate resist is therefore approximately three times more sensitive than PMMA to electron beams.

The contrast of a photoresist may also be determined from the plot of normalized thickness *versus* electron dose. It is defined as the slope of the linear portion of the curve extrapolated to intercept the normalized thickness = 1 line and the X-axis[21]. This slope is given by the equation:

$$\text{contrast} = \gamma = [\log(D_c/D_0)]^{-1}$$

where D_0 is the dose at which the developer begins to attack the irradiated film and D_c is the sensitivity. Contrast values are important, as they are related to the resolution that can be achieved in a resist and may be used to predict line profiles. It is generally desirable that the contrast of a resist be as large as possible. The values determined in the above examples were 3.5 and 4.2 for the 1.0 and 0.5 μm thick vapour coatings, respectively, and 4.1 for the spun-on resist. These values compare very

Figure 6 Illustration of the lithographic process: A, resist layer; B, thin dielectric layer (e.g. oxide); C, substrate; D, mask. Step 1, coat resist; step 2, expose; step 3, develop image; step 4, etch; step 5, strip resist
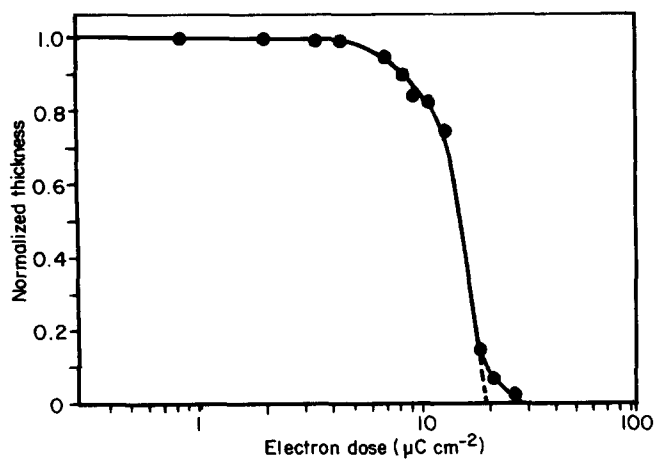
Figure 7 Sensitivity/contrast graph for 0.5 μm layer of vapour-deposited poly(ethyl-2-cyanoacrylate) developed using 3:2 blend of ethyl acetate/isobutyl methyl ketone
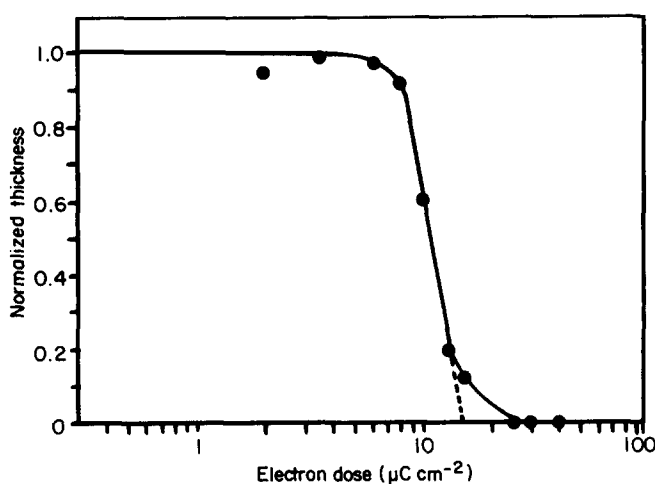

Figure 8 Sensitivity/contrast graph for 1.0 μm layer of vapour-deposited poly(ethyl-2-cyanoacrylate) developed using 3:2 blend of ethyl acetate/isobutyl methyl ketone
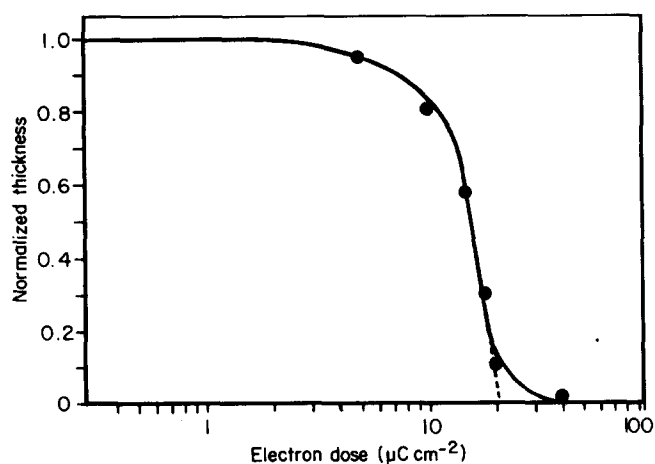

Figure 9 Sensitivity/contrast graph for 0.6 μm layer of spun-on poly(ethyl-2-cyanoacrylate) developed using 3:2 blend of ethyl acetate/isobutyl methyl ketone

favourably with PMMA, for which the contrast was found to be 2.0, measured using the same technique.

The nature of the alkyl side-chain substituent was found to have a marked influence on the sensitivity of the vapour-deposited cyanoacrylate resist. With increasing alkyl group size, the sensitivity was found to increase

significantly over the C_1 to C_4 range. Poly(methyl-2-cyanoacrylate) was found to have a sensitivity of $60 \mu C \, cm^{-2}$ whereas the corresponding value for poly(isobutyl-2-cyanoacrylate) was found to be $4 \mu C \, cm^{-2}$. A plot of log sensitivity *versus* molecular weight of the alkyl group for methyl, ethyl and isobutyl substituents suggests an inverse linear relationship (*Figure 10*).

The resist resolution was determined by exposing the test pattern, shown in *Figure 11*, in a vapour-deposited poly(ethyl-2-cyanoacrylate) resist layer grown on a silicon substrate. After exposure and development the imaged substrate was sectioned by cleaving along a crystal plane. The sectioned sample was then sputter-coated with ~ 10 nm of gold and inspected in a scanning electron microscope (SEM). This gives direct information on the line profiles as well as the actual dimension of the smallest resolved line. Some of the results obtained are presented in *Figures 12–17*.

Figure 12 shows excellent line profiles and good aspect ratios in 0.6, 0.8 and 1.0 μm lines (left to right) imaged in a 1.0 μm thick polymer layer. *Figure 13* shows a close-up of a 0.6 μm line in a 0.8 μm thick coating. *Figure 14* shows the 10, 5 and 2 μm lines in a 6 μm thick resist layer with good undercut. The undercutting is achieved by over-exposure to electron beams and is a very important resist requirement for processes involving 'metal lift-off'[20]. This process was used successfully to fabricate a working microwave transistor (MESFET) on gallium arsenide, where vapour-deposited poly(ethyl-2-cyanoacrylate) was used in all the masking steps. *Figure 15* shows the complete device with alignment marks, ohmic contacts, mesa structure and gate. *Figure 16* shows a close-up of gate metal running over the mesa step. The gate length on
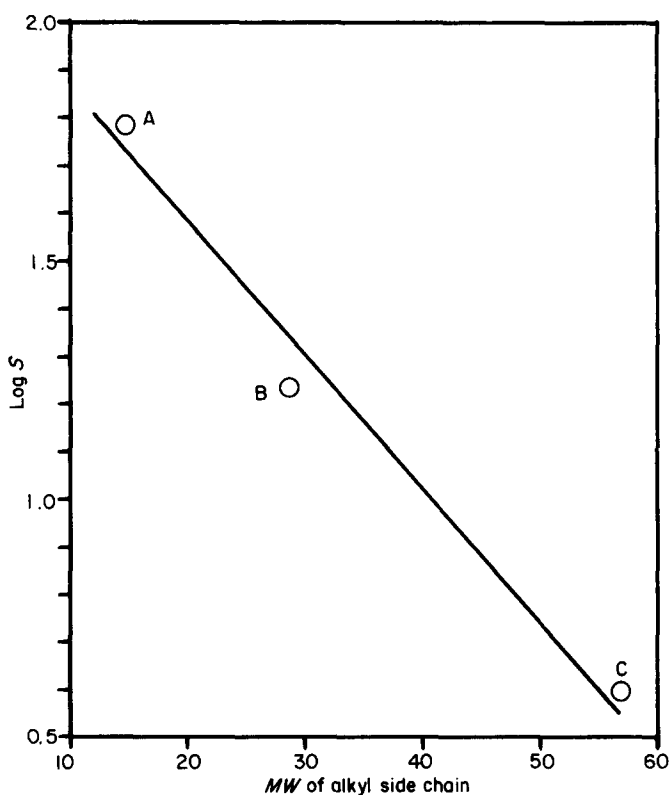

Figure 10 Logarithmic plot of sensitivity ($\mu C \, cm^{-2}$) *versus* molecular weight of alkyl side-chain in poly(alkyl-2-cyanoacrylates): A, methyl; B, ethyl; C, isobutyl

IO

300

5

IO

2

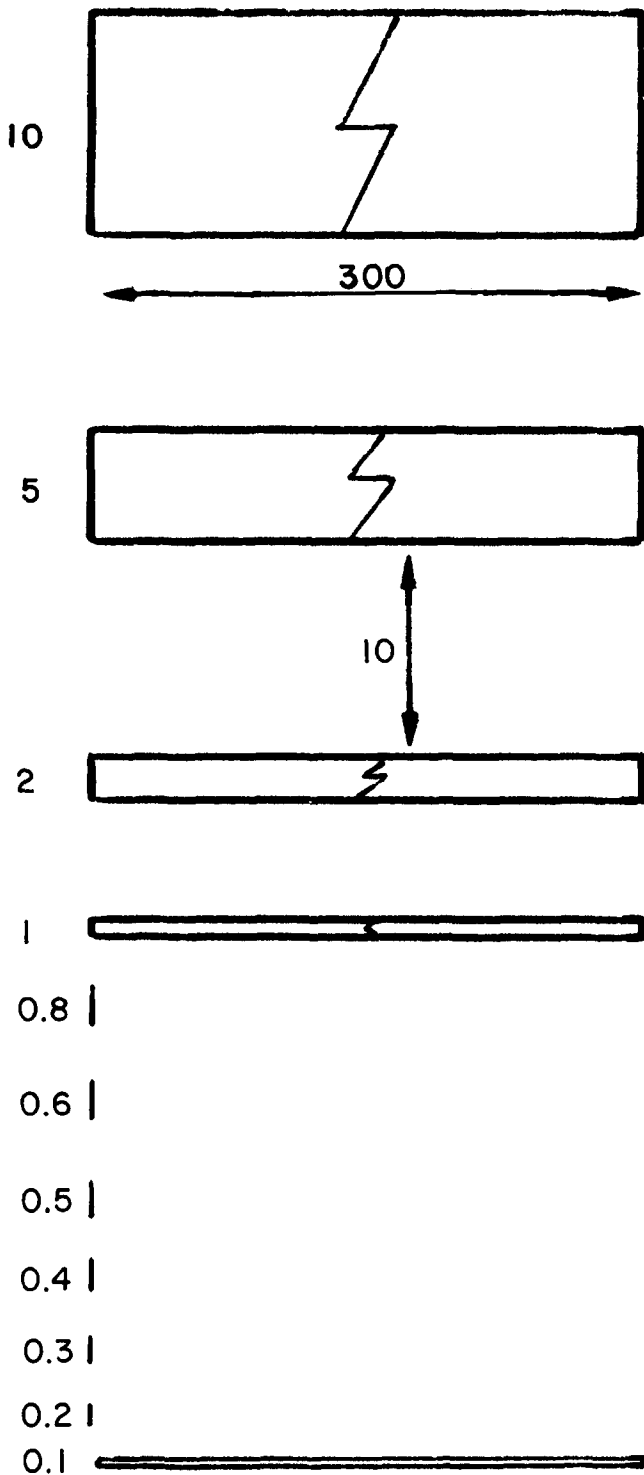**I**

0.8

0.6

0.5

0.4

0.3

0.2

0.1

Figure 11 Schematic diagram of the test pattern of lines and spaces used in resolution tests. All dimensions are in μm (not drawn to scale)

Figure 12 The 0.6, 0.8 and 1.0 μm lines (L to R) in 1.0 μm thick layer

Figure 13 Close-up of 0.6 μm lime in 0.8 μm thick film

Figure 14 The 10, 5 and 2 μm lines in 6 μm thick resist layer showing good undercut. The undercutting is necessary for processes involving 'metal lift-off' and is achieved by over-exposure
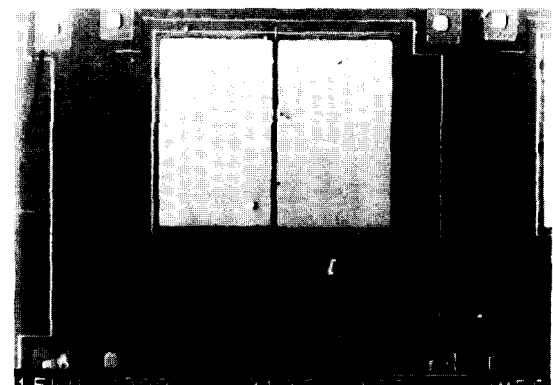
Figure 15 Working microwave transistor (MESFET) on gallium arsenide. Vapour-deposited poly(ethyl-2-cyanoacrylate) was used in all masking steps during fabrication. Photograph shows complete device with alignment marks, ohmic contacts, mesa structure and 0.7 μm gate metal. Bar = 100 μm

this device is 0.7 μm. The fabrication of this device demonstrated that vapour-deposited cyanoacrylate resists are compatible with conventional acidic wet etchants. Unlike spun-on resists, the vapour-deposited material does not form a planarizing layer but conformally coats steeply profiled features. The effect is clearly seen in *Figure 17* where there is no resist thinning over the coated steps.

As dry processing techniques are becoming more widespread in IC fabrication, so the plasma etch resistance of potential resists has become an increasingly
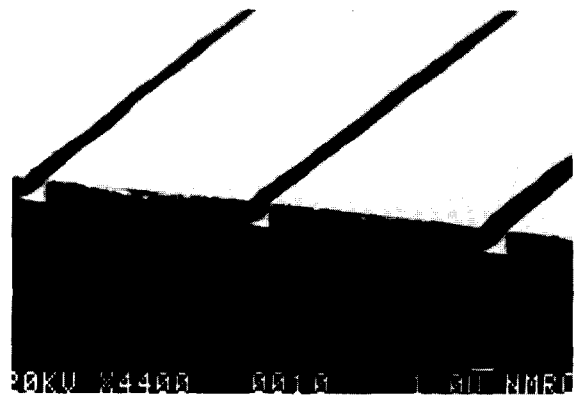
Figure 16 Close-up of gate metal running over mesa step
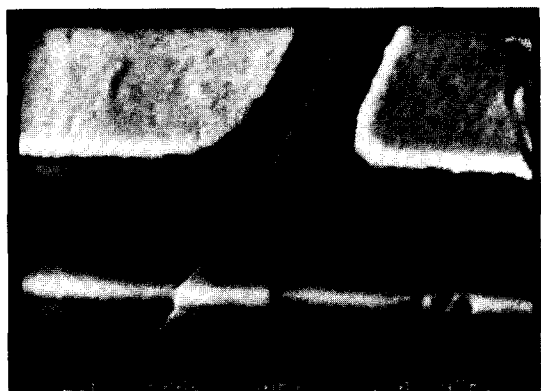

Figure 17 Conformal coating. Vapour-deposited poly(cyanoacrylate) resist film on steeply profiled features. Photograph shows no resist thinning over the coated steps, indicating conformal rather than planarizing coverage.

Table 1 Cyanoacrylate resist and oxide plasma etch rates: comparison with PMMA

Resist type	Application	Resist etch rate (Å min^{-1})	Oxide etch rate (Å min^{-1})	Resist/oxide etch rate ratio
Methyl	Vapour	40	80	0.5
Ethyl	Vapour	53	79	0.7
Isobutyl	Vapour	38	73	0.5
n-Butyl	Vapour	51	71	0.7
2-Methoxyethyl	Vapour	48	79	0.6
Ethyl	Spun	134	79	1.7
Isobutyl	Spun	100	85	1.1
n-Butyl	Spun	104	88	1.2
PMMA	Spun	103	79	1.3

important factor in resist selection. Since silicon dioxide is the most commonly used dielectric material in metal–oxide–semiconductor (MOS) technology, the plasma etch resistance of the vapour-deposited resists were measured relative to SiO_2. Samples prepared by depositing (vapour or spinning) resist polymer on clean $1 \times 1 \text{ cm}^2$ Si wafers, along with similar substrates containing sputtered oxide, were plasma-etched for 10 min. The residual resist and oxide layer thickness was then measured and the etching rates calculated. The results obtained are presented in *Table 1*.

A resist/oxide etch rate ratio less than 1.0 is desirable if the resist is to have adequate plasma etch resistance for most applications. It is clear from the data in *Table 1* that vapour-deposited cyanoacrylate resists have significantly better plasma etch resistance over the equivalent solution-spun materials and over PMMA. The reason for this improvement is not yet understood, but may be related to differences in molecular weight, crystallinity, tacticity or density of the polymers, and these aspects are currently under investigation. Also under investigation is the resistance of the vapour-deposited film to reactive ion etching (RIE). This dry etching technique is becoming an increasingly important feature in IC fabrication processes.

The foregoing discussion has been concerned with E-beam lithography. A preliminary examination has shown that deep-u.v. radiation may also be used to image vapour-deposited cyanoacrylate resist layers, and characterization studies are currently in progress.

CONCLUSIONS

A new method for the deposition of poly(alkyl-2-cyanoacrylate) resists has been developed which involves the growth of a polymeric film, on an activated semiconductor surface, directly from the monomer vapour. The entire process may be carried out at ambient or near-ambient temperatures and at atmospheric pressure. The method avoids the use of solvents and, by comparison with conventional spin coating techniques, allows the deposition of relatively thick films to be made. The resist films prepared by this method have been shown to be useful as electron-beam resists, with benefits in sensitivity, contrast and dry etch resistance over PMMA, which is at present the most common E-beam resist in use. Preliminary work has shown that the vapour-deposited films may also be used as deep-u.v. photoresists.

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